

# Table of Contents

Acknowledgements .....	i
Abstract.....	vii
Kurzfassung .....	xi
Table of Contents .....	xv
Chapter 1 - Introduction.....	1
1.1. General introduction.....	1
1.2. Objective of the thesis .....	4
1.3. Structure of the thesis.....	6
Chapter 2 - State of the Art.....	9
Part I : Chlorides and their role in reinforced concrete.....	9
2.1. Measuring concrete’s resistance to chloride ingress .....	10
2.2. Measuring chloride ions in concrete.....	15
2.2.1. Qualitative colorimetric indicator .....	15
2.2.2. Acid-soluble chloride content- quantitative analysis .....	16
2.2.3. X-ray fluorescence spectroscopy- quantitative analysis.....	16
2.2.4. Ion selective electrodes.....	17
2.3. Spatial variability of chloride front and its importance in the new, trending field of digitally fabricated concrete .....	18
Part II : Background – data collection and processing.....	22
2.4. X-Ray Fluorescence .....	22
2.4.1. Principles of X-ray fluorescence .....	23

2.4.2. Analytical precision and accuracy in X-ray Fluorescence Analysis	25
2.4.3. Specimen preparation	27
2.4.3.1. Solid specimens	28
2.4.3.2. Powdered specimens	28
2.4.4. Quantitative analysis in X-ray fluorescence	29
2.4.5. Micro X-ray fluorescence	32
2.5. Data processing using Support Vector Machines	35
2.5.1. Linearly separable binary classification	35
2.5.1.2. The mathematics	36
2.5.2. Nonlinear Support Vector Machines	41
2.5.2.2. The Kernel Trick	42
Chapter 3 - Method Development and Validation	47
3.1. Introduction	47
3.2. Experimental	50
3.2.1. Materials	50
3.2.2. Standard and sample preparation	54
3.2.3. Instrumentation	56
3.2.3.1. Detectors	56
3.2.3.2. Measurement protocol	56
3.2.4. Method Validation	57
3.2.5. Support Vector Machines	58
3.3. Results and discussion	59
3.3.1. Calibration curve for D1	59
3.3.2. Calibration curve for D2	61
3.3.3. Limits of detection and quantification	62
3.3.4. Method performance	63
3.3.5. Comparison with established quantification technique used in practice	67
3.3.6. Method performance with a different w/c	68
3.3.7. Method performance regarding different cements	71
3.3.8. SVM performance versus linear method	73
3.3.9. Relevance of the method	76
3.4. Conclusions	77
Chapter 4 – Application: Insight into basic transport processes of chlorides	79
4.1. Introduction	79

4.2. Experimental	81
4.2.1. Materials	81
4.2.2. Diffusion experiments	82
4.2.2.1. Sample preparation	82
4.2.2.2. Method	84
4.2.3. Capillary rise	85
4.2.3.1. Sample preparation	85
4.2.3.2. Method	87
4.2.4. Ion selective electrodes	88
4.2.5. Micro XRF	90
4.2.5.1. Diffusion samples	90
4.2.5.2. Capillary suction samples	90
4.3. Results	91
4.3.1. Diffusion transport	91
4.3.1.1. High water cement ratio (WC1= 0.6)	91
4.3.1.2. Low(er) water cement ratio (WC2= 0.45)	97
4.3.2. Capillary rise	102
4.4. Discussion	107
4.4.1. Diffusion experiment	107
4.4.2. Capillary rise experiment	110
4.5. Conclusions	114
Chapter 5 – Chloride Ingress Through Cold Joints in Digitally Fabricated Concrete	117
5.1. Introduction	117
5.2. Materials and Methods	120
5.2.1. Materials for the 3D printed samples	120
5.2.2. Materials for the chloride exposure	121
5.2.3. Preparation of 3D Printed samples	121
5.2.4. Chloride exposure	124
5.2.5. Moisture ingress by neutron imaging	125
5.2.6. Instrumentation	126
5.2.6.1. Micro XRF	126
5.2.6.2. Neutron imaging and analysis	127
5.3. Results	128
5.3.1. Chloride maps	128
5.3.2. Neutron imaging of moisture	130

5.4. Discussion .....	132
5.5. Conclusions and Outlook .....	139
Chapter 6 - Global Conclusions and Outlook.....	141
6.1. Main Outcomes.....	141
6.2. Outlook.....	144
References.....	149
Appendix A – Original Plan .....	161
A.1. Original objective .....	161
A.2. State of the art for mathematical modeling of chloride transport in concrete .....	162
A.3. Limitations of simplified models .....	163
A.3.2. Free versus bound chlorides.....	168
A.3.2.1. Thermodynamic Modeling .....	168
A.4. Experimental technique .....	170
A.4.1. Analytical methodology for quantitative high spatial resolution chemical imaging based on micro-X-ray fluorescence.....	172
A.4.2. Strategy.....	173
A.4.3. Preliminary Experiments .....	177
A.5. References .....	180
Appendix B : Standards preparation development .....	185
CURRICULUM VITAE.....	189